Collective and single particle correlations in a binary mixture : dependence on the mass ratio

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I. **Nonlinear Fluctuating Hydrodynamics**

for dense liquids.

Self generated SLOW DYNAMICS

II. Binary Mixture :

Collective and Single-particle correlations

Mass ratio dependence

III. Dynamical Heterogeneities

Higher order correlations

A. Density Functional Theory for metastable states

B. Configurational entropy and packing of a hard sphere system

Statistical Mechanics of many particle systems

Perturbation around a basic reference state

Low density Gas : large mean free path

Solid : Underlying Crystalline structure

DENSE LIQUIDS APPROACHING GLASS TRANSITION

NO SUCH REFERENCE STATE

Microscopic theory for the formation of the self generated disordered solid.

Isotropic liquid

Dynamics of the slow modes

due to conservation laws.

Mass, Momentum Fluctuations

around the Equilibrium state

$$\hat{\rho}(\mathbf{x},t) = \sum_{\alpha} m\delta(\mathbf{x}-\mathbf{r}_{\alpha}),$$

$$\hat{\mathbf{g}}_i(\mathbf{x},t) = \sum_{\alpha} p_{\alpha}^{i}\delta(\mathbf{x}-\mathbf{r}_{\alpha}).$$

Represents the microscopic conservation laws.

COARSE GRAINED DENSITIES :

Stochastic equations

LINEAR DY

$$\frac{\partial \rho}{\partial t} + \nabla.\mathrm{g} = 0$$

.

$$\frac{\partial g_i}{\partial t} + c_0^2 \nabla_i \rho + \Gamma_0 \nabla^2 g_i = \theta_i$$

Broken symmetry : Goldstone modes

Time correlation functions

Equilibrium average over initial conditions

Average over noise in stochastic equations

$$C_{ab}(t,t') = < \delta\hat{\psi}_a(t)\delta\hat{\psi}_b(t') >$$

Low density Fluids

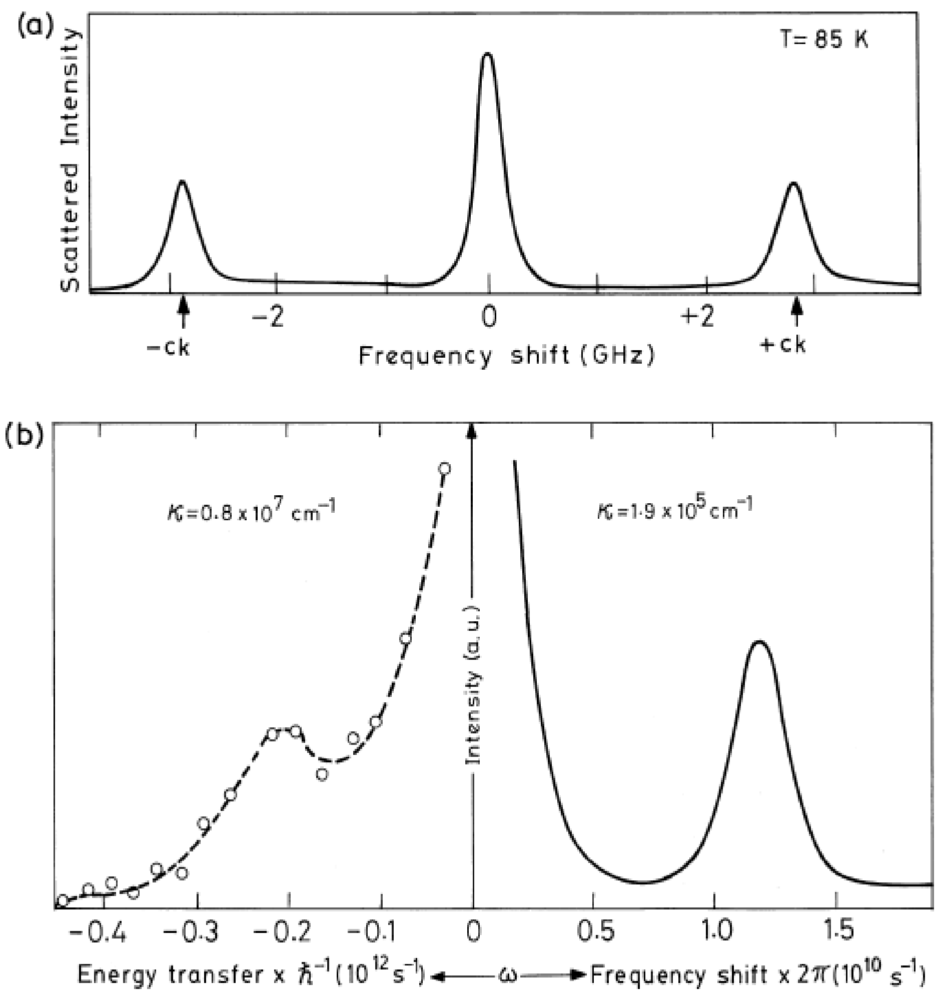
Linear equations of are sufficient for describing the dynamics and relaxation to equilibrium.

$$\left[\frac{\partial^2}{\partial t^2} + \Gamma_0 q^2 \frac{\partial}{\partial t} + c_0^2 q^2\right] G_{\rho\rho}(q,t) = 0$$

Short time (bare) transport coefficients: Boltzmann or Enskog level description

Linear Fluctuating Hydrodynamics

Dynamics of collective modes



$$\psi(q,z) = \left[z - \frac{\Omega_q^2}{z + iq^2\Gamma_0} \right]^{-1},$$

$$z = \pm q c_o + \frac{i}{2}\Gamma_0 q^2,$$

Propagating sound modes with attenuation

The Supercooled liquid

Correlated motion of the fluid particles at high density.

Cage effect **Small Diffusion coefficient D of a Tagged particle.**

•Particles get trapped in a cage of surrounding particles.

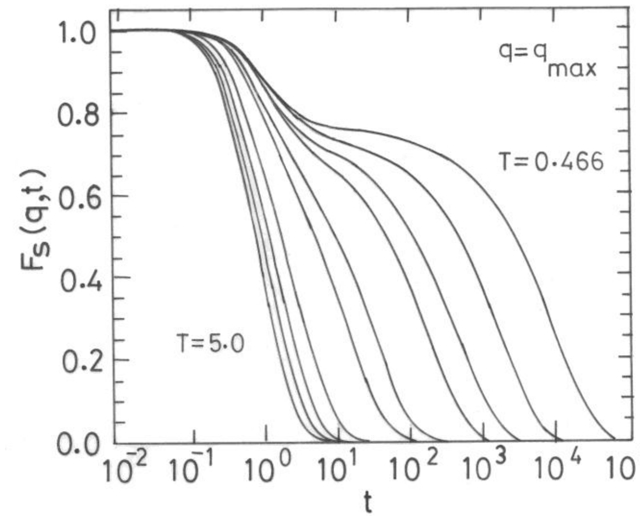
•*Glass transition* – Jamming of the

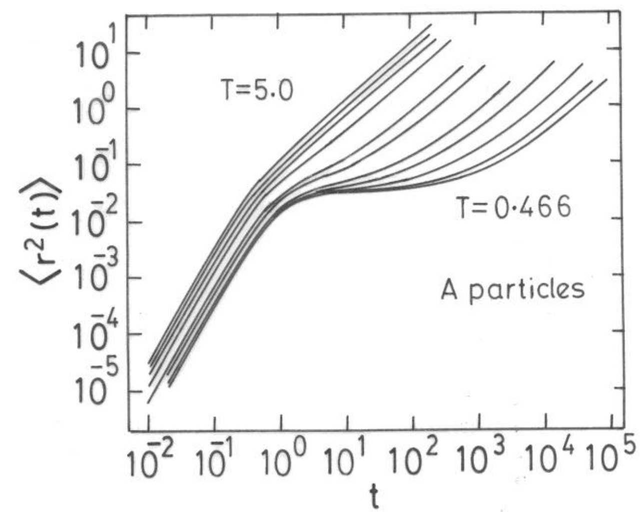
•particles in the amorphous structure.

•D→0 and

Very long relaxation times.

(W. Kob and H.C. Anderson)





Nonlinear Fluctuating Hydrodynamics

Generalized Langevin equations

$$\frac{\partial \hat{\phi}_i(t)}{\partial t} = V_i[\hat{\phi}] - \sum_j L^0_{ij} \frac{\partial F}{\partial \hat{\phi}_j} + \theta_i(t) \quad ,$$

$$\rho(x,t) \qquad g(x,t)$$

$$< \theta_i(t)\theta_j(t') >= 2k_B T L^0_{ij} \delta(t-t')$$

Mass density , Momentum density

Fluctuating equations for the slow variables

Isotropic Liquid

$$\frac{\partial \rho}{\partial t} + \nabla.\mathrm{g} = 0$$

$$\frac{\partial g_i}{\partial t} = -\rho \nabla_i \frac{\delta F_U}{\delta \rho} - \sum_j \nabla_j (\frac{g_i g_j}{\rho}) + \sum_j L^o_{ij} \frac{g_j}{\rho} + f_i \ .$$

At high density :

Cooperative motion of the liquid particles.

Coupling of the hydrodynamic modes.

.

Plausible generalizations of the laws of hydrodynamics

Two approaches

Equations of Fluctuating Nonlinear Hydrodynamics (FNH)

I. Correction due to the nonlinear coupling of the slow modes

Field theoretic methods : Perturbative corrections to

transport properties at Lowest order

Mode Coupling theory (MCT)

Critical Phenomena : Kawasaki, Kadanoff-Martin

Self-consistent MCT – for Glassy Dynamics : W. Gotze

II. Direct solution of the equations of FNH

(G. Mazenko and O. Valls, C. Dasgupta and O. Valls,

Sen Gupta, Das and Barrat,)

Feedback mechanism from density fluctuations

Enhancement of relaxation times : Slow dynamics

The Self-consistent mode coupling theory

Order Parameter to mark the ergodicity-nonergodicity transition →

$$\psi(\mathbf{x}, t) \equiv \delta\rho(\mathbf{x}, t)\delta\rho(\mathbf{x}, 0)$$

$$\lim_{t\to\infty} \langle \delta\rho(\mathbf{x}, t)\delta\rho(\mathbf{x}, 0)\rangle = \lim_{t\to\infty} \langle \psi(\mathbf{x}, t)\rangle = 0.$$

Ergodic: LONG TIME LIMIT of ψ(t) ⟶ 0

ERGODICITY-NONERGODICITY Transition : Nonzero ψ(t)

LONG TIME LIMIT of Single-particle correlation function $\psi_s(t)$ is simultaneously frozen at the ENE Transition point. Ds=0

Cross over in the dynamics.

Extrapolated self diffusion Ds → 0

The tagged particle correlation decays to zero beyond ENE transition in our model.

The Self-consistent mode coupling theory

Density Correlation function expressed in terms of the Memory function L(q,z)

$$\psi(q,z) = \left[z - \frac{\Omega_q^2}{z + iq^2 L(q,z)} \right]^{-1},$$

ONE-LOOP approximation

$$L(q,z) \equiv \mathcal{M}_q[\{\psi\}]. \longrightarrow m(z) = m_0 + \int_0^\infty dt\, e^{izt} c_2 \psi^2(t),$$

$$\phi(q,t) = f(q) + [1 - f(q)]\phi_v(q,t).$$

$$\frac{f_q}{1-f_q} = \frac{1}{\Omega_q^2}\tilde{m}^L(q, t \to \infty) \equiv \mathcal{H}_q[f_k],$$

U Bengtzelius, W Götze and A Sjölander

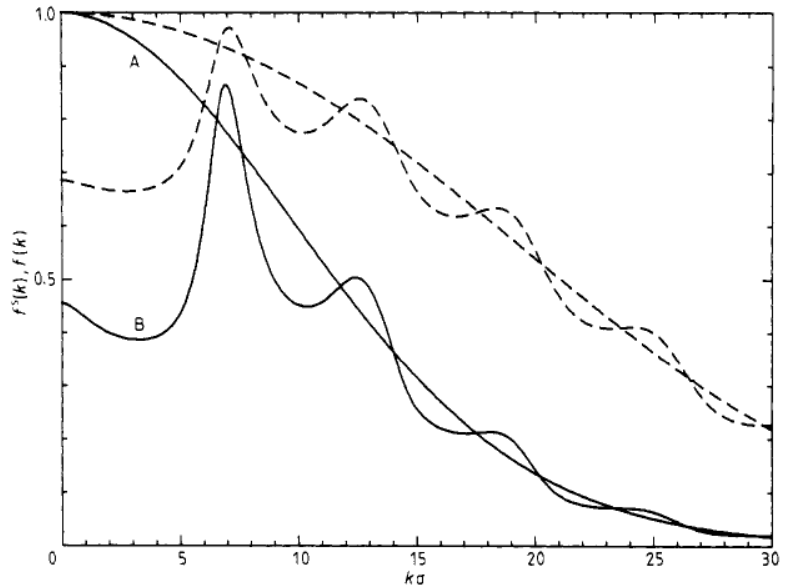


Figure 2. The form factors $f^s(k)$ (A) and $f(k)$ (B) at a packing fraction $\eta = 0.516$ (full curves) and $\eta = 0.550$ (broken curves).

ERGODICITY -NONERGODICITY TRANSITION occur AT PACKING FRACTION .524 in a HARD SPHERE SYSTEM in the simple model

JAMMING OF THE SYSTEM at low packing fraction

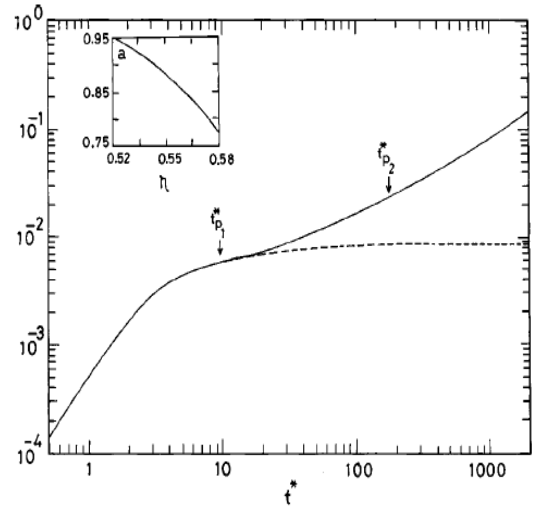
Single-particle correlation function $\psi_s(t)$: Self diffusion constant goes to zero

LONG TIME LIMIT of $\psi_s(t)$ is frozen at the ENE Transition point

$$\psi(q,z) = \left[z - \frac{\Omega_q^2}{z + iq^2 L(q,z)} \right]^{-1},$$

$$\psi_s(q,z) = \frac{1}{z - \frac{v_o^2 q^2}{z + i\Gamma_s(\vec{q},z)}},$$

$$\Gamma_s^{mc}(q,t) = \frac{n}{\beta m} \int \frac{d\vec{k}}{(2\pi)^3} \psi_s(|\vec{q}-\vec{k}|,t) V_s(\vec{q}-\vec{k},\vec{k}) \psi(k,t),$$



Momentum density for the tagged particle is not a conserved property like its number

Self diffusion

Tagged particle density is a conserved property but not its momentum density .

The equations of fluctuating Nonlinear hydrodynamics

Binary mixtures

$$\rho(\mathbf{x},t) = \rho_1(\mathbf{x},t) + \rho_2(\mathbf{x},t),$$
$$c(\mathbf{x},t) = x_2\rho_1(\mathbf{x},t) - x_1\rho_2(\mathbf{x},t)$$

The equations of fluctuating Nonlinear hydrodynamics

$$\frac{\partial\rho}{\partial t} + \nabla.\mathbf{g} = 0,$$
$$\frac{\partial \mathrm{g}_i}{\partial t} + \sum_j \nabla_j\left[\mathrm{g}_i \mathrm{v}_j\right] + \rho\nabla_i\frac{\delta F_u}{\delta\rho} + c\nabla_i\frac{\delta F_u}{\delta c} + \sum_j L^0_{ij}\mathrm{v}_j = \theta_i,$$
$$\frac{\partial c}{\partial t} + \nabla\cdot\left[c\mathbf{v}\right] + \gamma_0\nabla^2\frac{\delta F_u}{\delta c} = f \quad ,$$

One component limit of the binary system : Proper accounting of the conservation laws

For the binary mixture the correlations of total density (ρ) and concentration (c) freeze at the ENE transition.

In the One component limit of the mixture the tagged particle correlation decays to zero. Only the total density Correlation freeze at the ENE transition.

Self diffusion is not Zero.

PRE 92 062308 (2015), PRE 92 062309 (2015)

Adiabatic approximation

NON-ERGODICITY PARAMETER WITH ADIABATIC APPROXIMATION

In the deeply super-cooled state the momentum density relaxes much faster than the density fluctuations : adiabatic approximation

Over-damping limit (Kyozi Kawasaki, 2000)

$$\frac{\partial g_i}{\partial t} = -\rho \nabla_i \frac{\delta F_U}{\delta \rho} - \sum_j \nabla_j \left(\frac{g_i g_j}{\rho}\right) + \sum_j L_{ij}^o \frac{g_j}{\rho} + f_i \ .$$

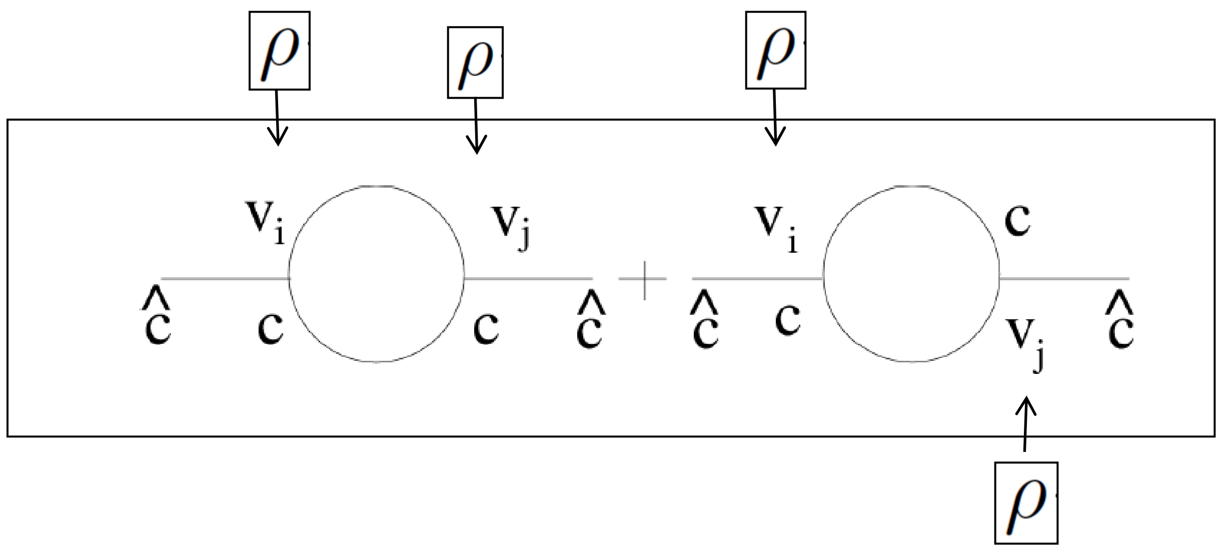
NON-ERGODICITY PARAMETER WITH ADIABATIC APPROXIMATION

Adiabatic approximation

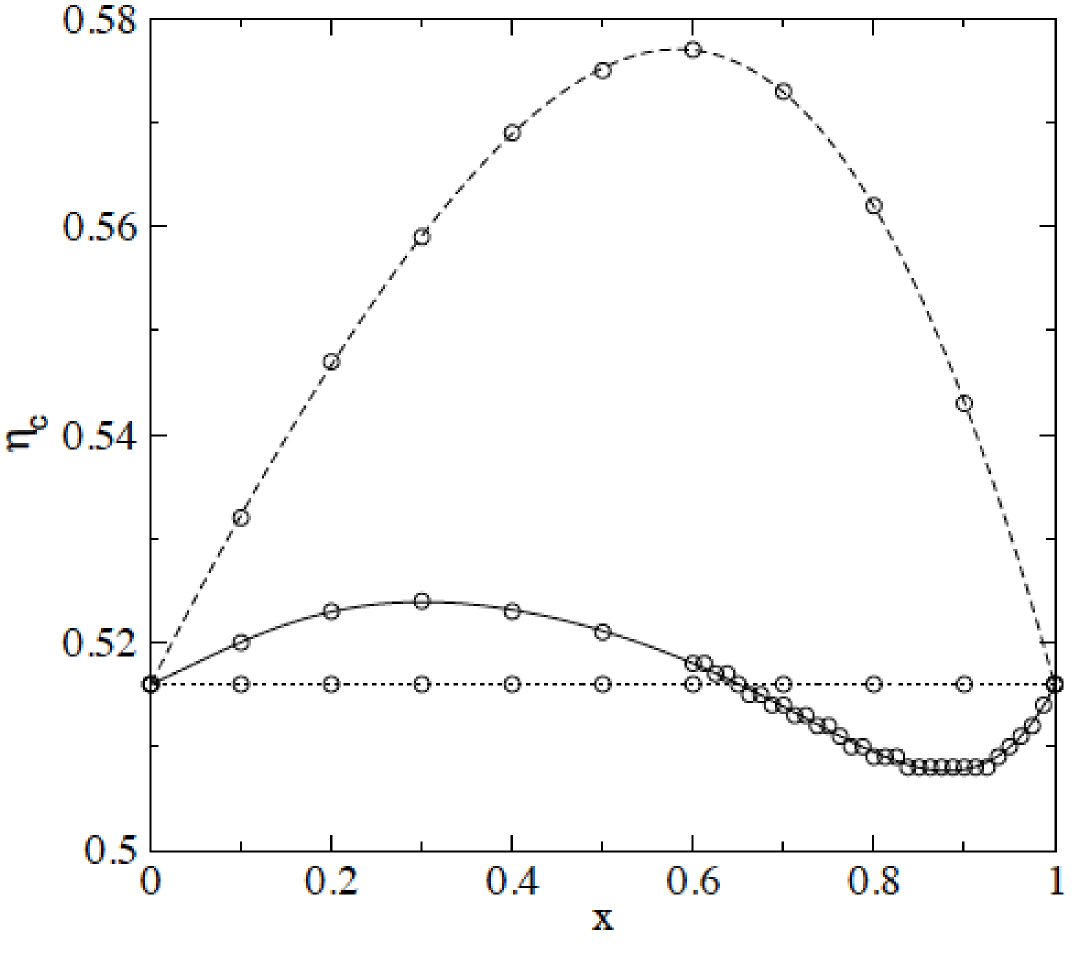
Binary Mixture

$$\nabla_j(\rho v_i v_j) + \rho\nabla_i \frac{\delta \tilde{F}_U}{\delta \rho} + \rho \frac{\delta \tilde{F}_U}{\delta c} - \sum_j \Gamma^0_{ij} \mathrm{v}_j = \theta_i$$

$$\begin{aligned}
\Gamma_0^2(k) G_{v_i v_j}(k) &= \left(\frac{\rho_0}{\beta m^2}\right)^2 k_i k_j \left[c_{\rho\rho}^2 G_{\rho\rho}(k) + c_{\rho\rho} c_{\rho c}\{G_{\rho c}(k) + G_{c\rho}(k)\} + c_{\rho c}^2 G_{cc}(k)\right] \\
\Gamma_0(k) G_{v_i c}(k) &= i \frac{\rho_0}{\beta m^2} k_i \{c_{\rho\rho}(k) G_{\rho c}(k) + c_{\rho c}(k) G_{cc}(k)\}
\end{aligned}$$



Transition for the binary mixture



One component system : Self diffusion

U Bengtzelius, W Götze and A Sjölander

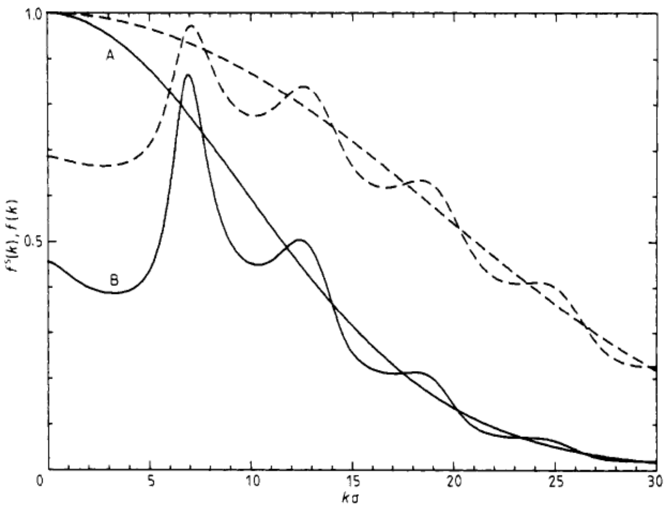
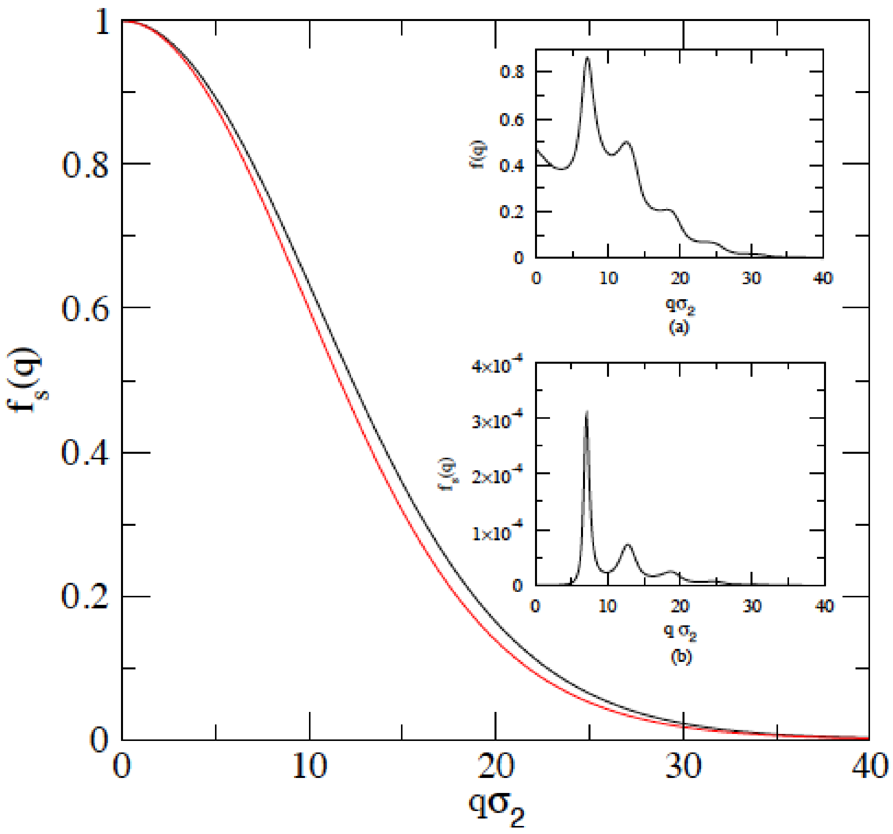


Figure 2. The form factors $f^s(k)$ (A) and $f(k)$ (B) at a packing fraction $\eta = 0.516$ (full curves) and $\eta = 0.550$ (broken curves).



In general the self diffusion coefficient is not zero at the ENE transition point, at which the collective density correlation freeze. Self diffusion is nonzero.

In the **adiabatic approximation** we find that the tagged particle Correlation gets frozen at the Ergodicity-non-ergodicity (ENE) transition point and self diffusion is zero.

**Microscopic momentum conservation plays a key role

Earlier MCT model equations follow from

$$\frac{\partial \rho_s}{\partial t} + \nabla \cdot \vec{g}_s = 0$$

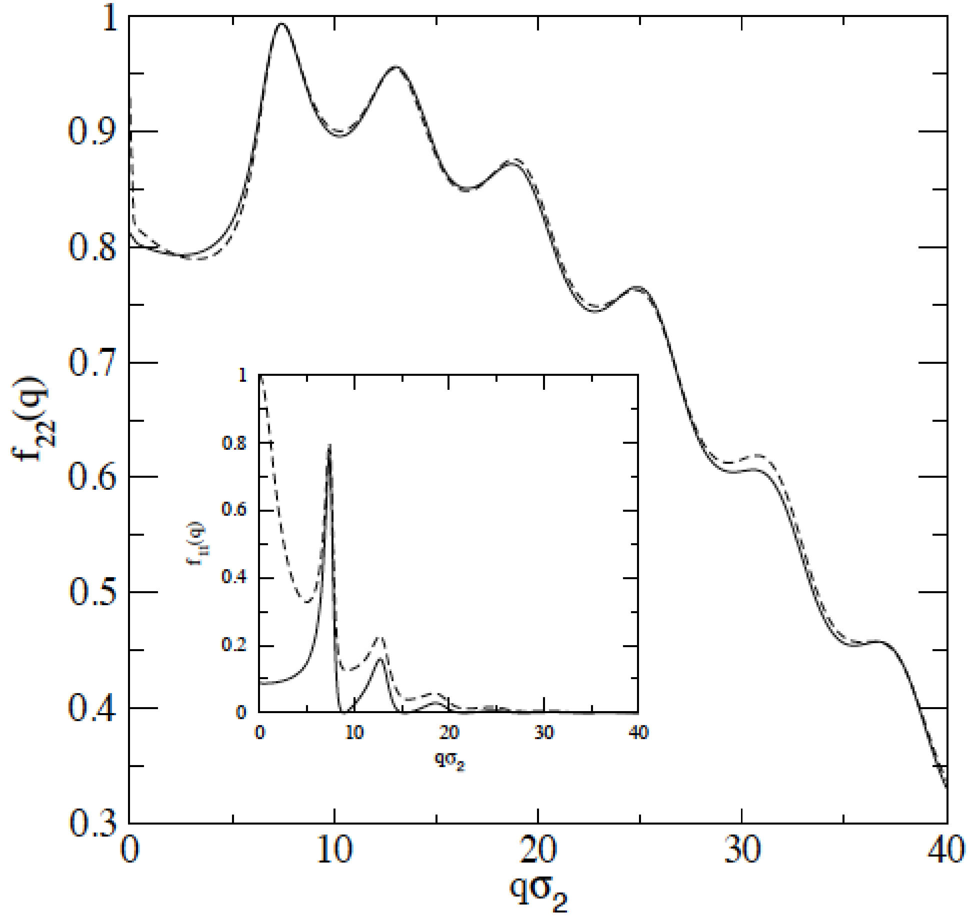
$$\rho_s(\vec{x}) = m_s \sum_{\alpha=1}^{N_s} \delta(\vec{x} - \vec{R}_s^{\alpha}(t))$$

$$\frac{\partial g_{is}}{\partial t} + \nabla_j \frac{g_{is} g_{js}}{\rho_s} + \rho_s \nabla_i \frac{\delta F_u}{\delta \rho_s} + Ł_{ij}^{ss'} \frac{\delta F}{\delta g_{js'}} = \tilde{f}_{is}$$

$$\vec{g}_{is}(\vec{x}) = \sum_{\alpha=1}^{N_s} \vec{P}_{is}^{\alpha} \delta(\vec{x} - \vec{R}_s^{\alpha}(t)) \quad s = 1,2$$

Density correlations and current correlations behave similarly (Das and Mazenko, 2009)

Brownian Limit of the mixture



Mass Ratio Dependence

DOI: 10.1103/PhysRevLett.92.225703

VOLUME 92, PHYSICAL REVIEW LETTERS week ending 4 JUNE 2004

Is There a Reentrant Glass in Binary Mixtures?

E. Zaccarelli,[1,2] H. Löwen,[2] P. P. F. Wessels,[2] F. Sciortino,[1] P. Tartaglia,[1] and C. N. Likos[2]

From its basic formulation, the two-component mode-coupling theory (MCT) for the ideal glass transition [14] asserts that the latter depends only on the static partial structure factors of the mixture and, hence, it is independent on the individual short-time mobilities [15]. This assertion holds both for Brownian dynamics (relevant for colloid/polymer mixtures) and for Newtonian short-time dynamics (relevant for molecular glass formers). Our computer simulation studies reveal, however, that the scenario and the location of the glass transition in the mixture depends crucially on the ratio α between the short-time mobilities of the glass-forming component and of the additive. We also show that MCT correctly

[15] A recent MCT version shows a mass ratio dependence of the glass transition point. See U. Harbola and S. P. Das, Phys. Rev. E **65**, 036138 (2002); J. Stat. Phys. **112**, 1109 (2003).

The mass ratio dependence drops out in the earlier model.

The ENE transition point depends the on mass ratio.

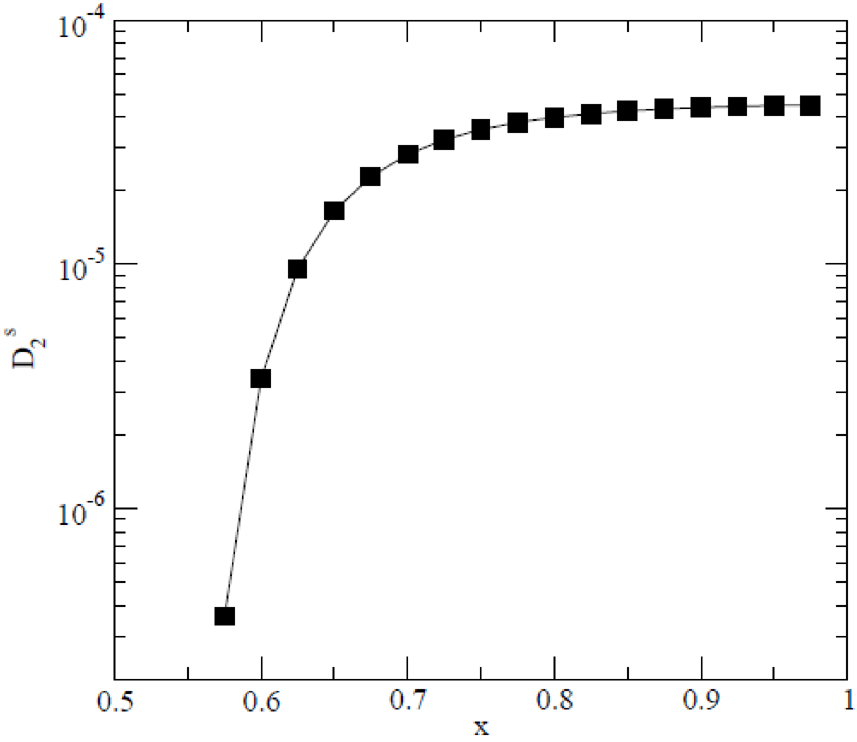
(Harbola and Das 2003)

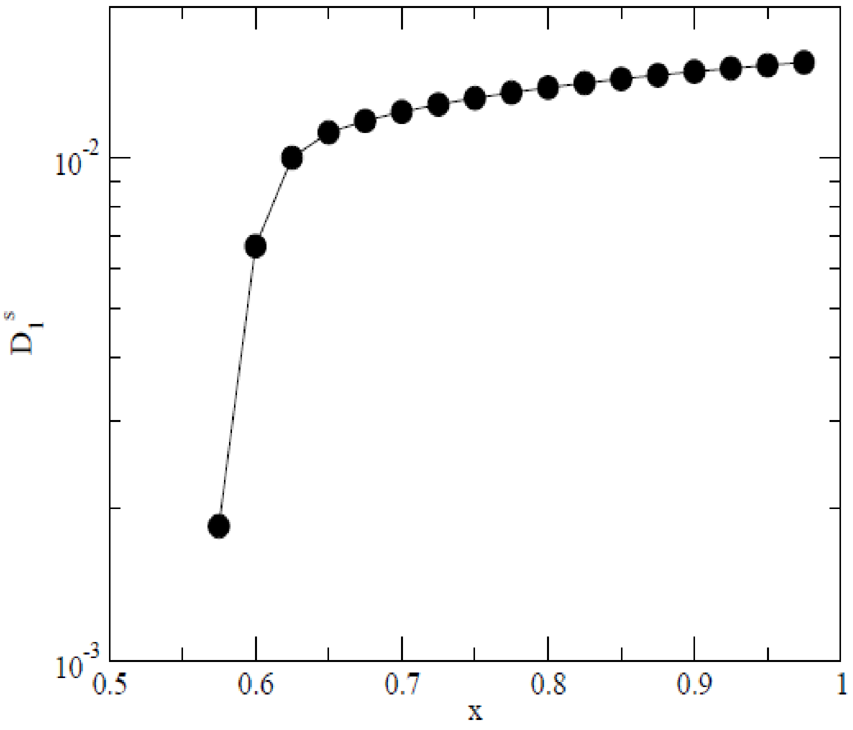
Tagged particle diffusion depends on mass ratio.

We apply adiabatic approximation.

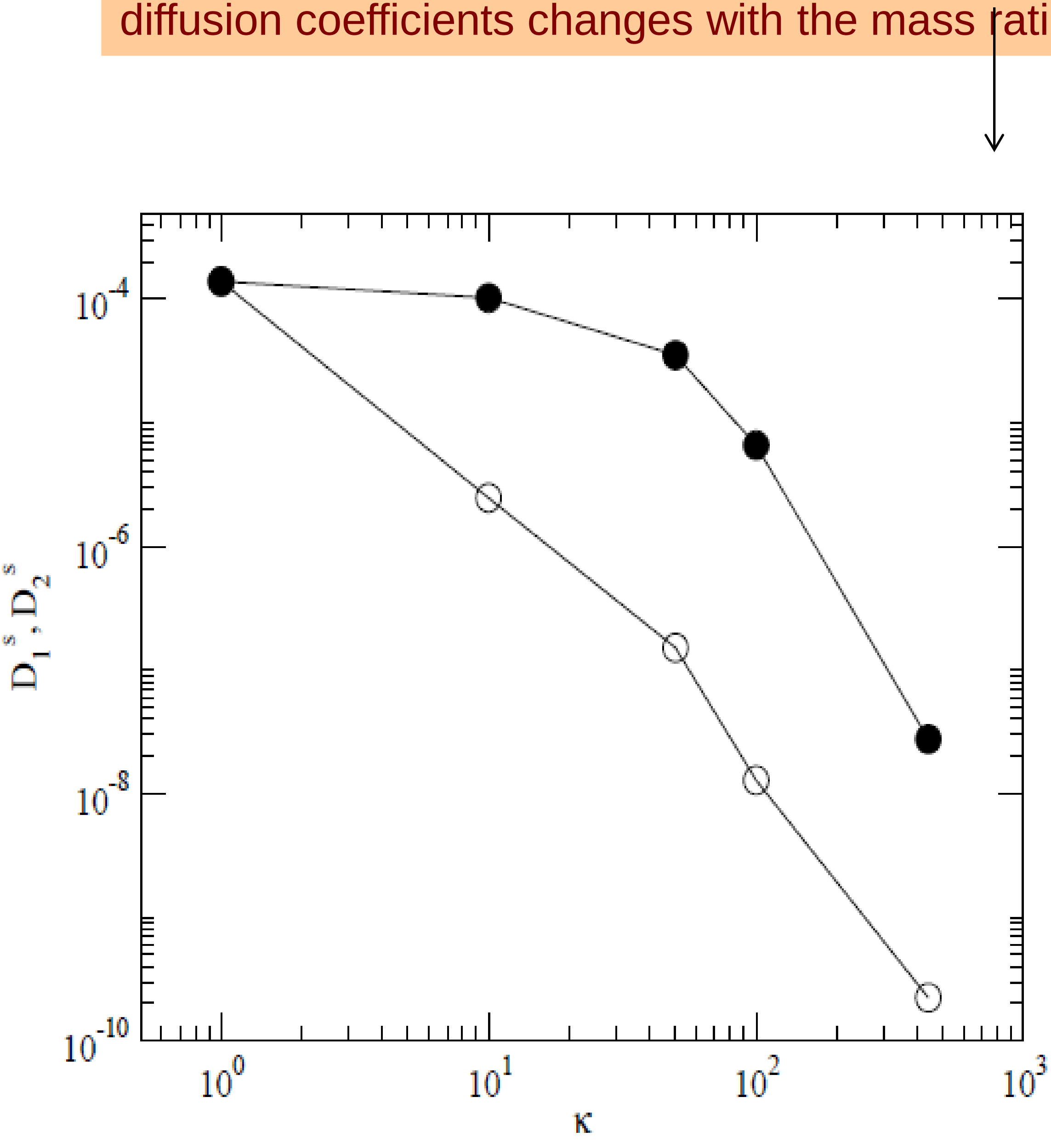
(Bidhhodi and Das 2017)

Self diffusion coefficients change with concentration of bigger particles at fixed mass ratio 10 and size ratio =0.5

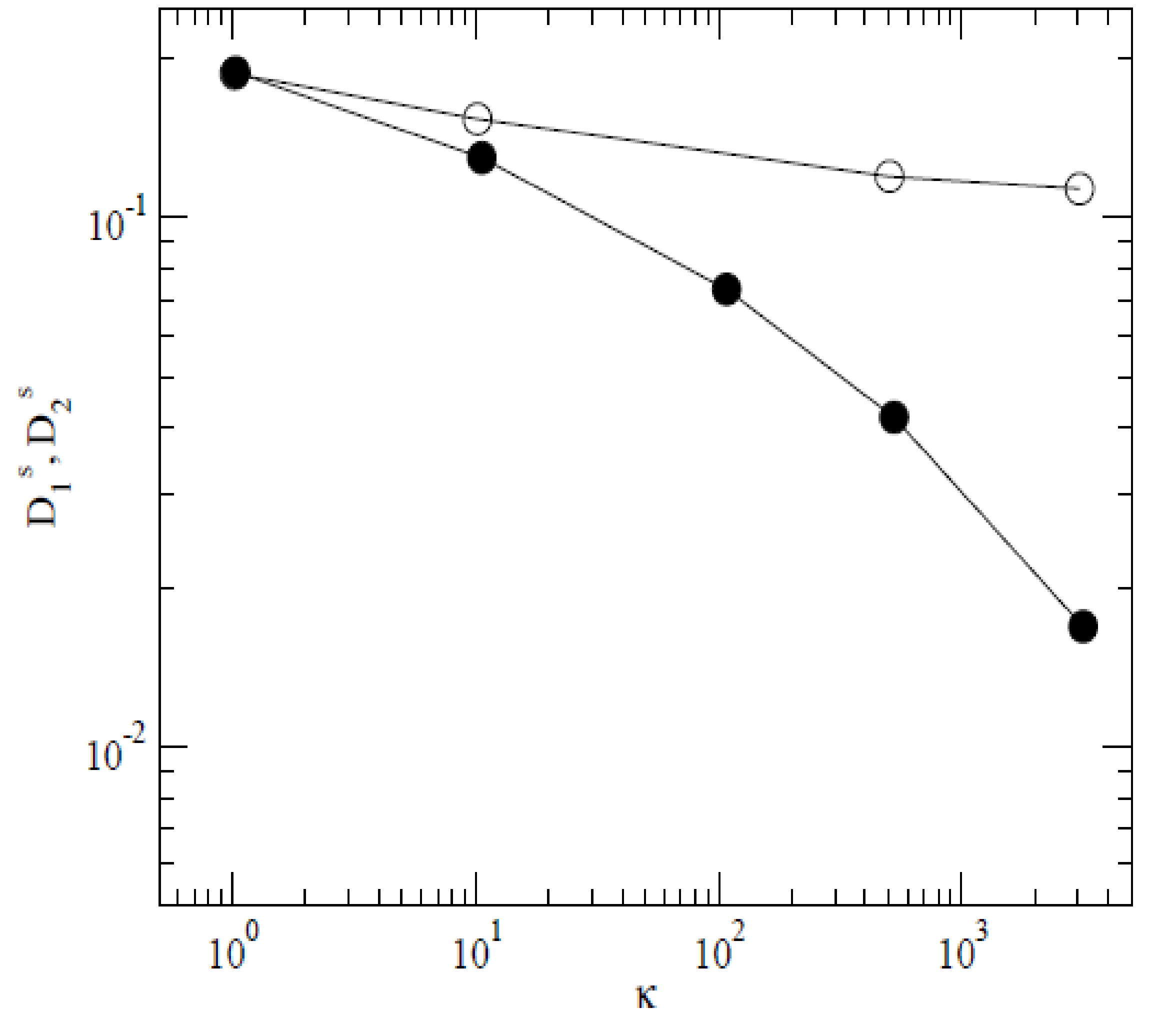




For fixed concentration x=.95 of the spheres the self diffusion coefficients changes with the mass ration



Soft Sphere (x=.2) diffusion coefficients with mass ratio
Simulations by Fenz et. al. PRE 80 021202 (2009)



Density Functional Model

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} \left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}} e^{-\alpha|\mathbf{r}-\mathbf{R_i}|^2} \equiv \sum_{i=1}^{N} \phi(\mathbf{r} - \mathbf{R}_i)$$

$$f_{\rm id}[\rho(\mathbf{r})] = N^{-1} \int d\mathbf{r} \rho(\mathbf{r}) \left(\ln[\rho(\mathbf{r})\Lambda^3] - 1\right),$$

The Weighted density functional

$$\bar{\rho}(\mathbf{x}) = \int d\mathbf{x}' w[\mathbf{x} - \mathbf{x}'; \bar{\rho}(\mathbf{x})]\rho(\mathbf{x}').$$

$$2f'_{\rm ex}(\hat{\eta})\hat{\eta} = -\eta\hat{\eta}f''_{\rm ex}(\hat{\eta}) - N^{-1} \int d\mathbf{x} \int d\mathbf{x}' \rho(\mathbf{x})\rho(\mathbf{x}')c(|\mathbf{x} - \mathbf{x}'|; \hat{\eta})$$

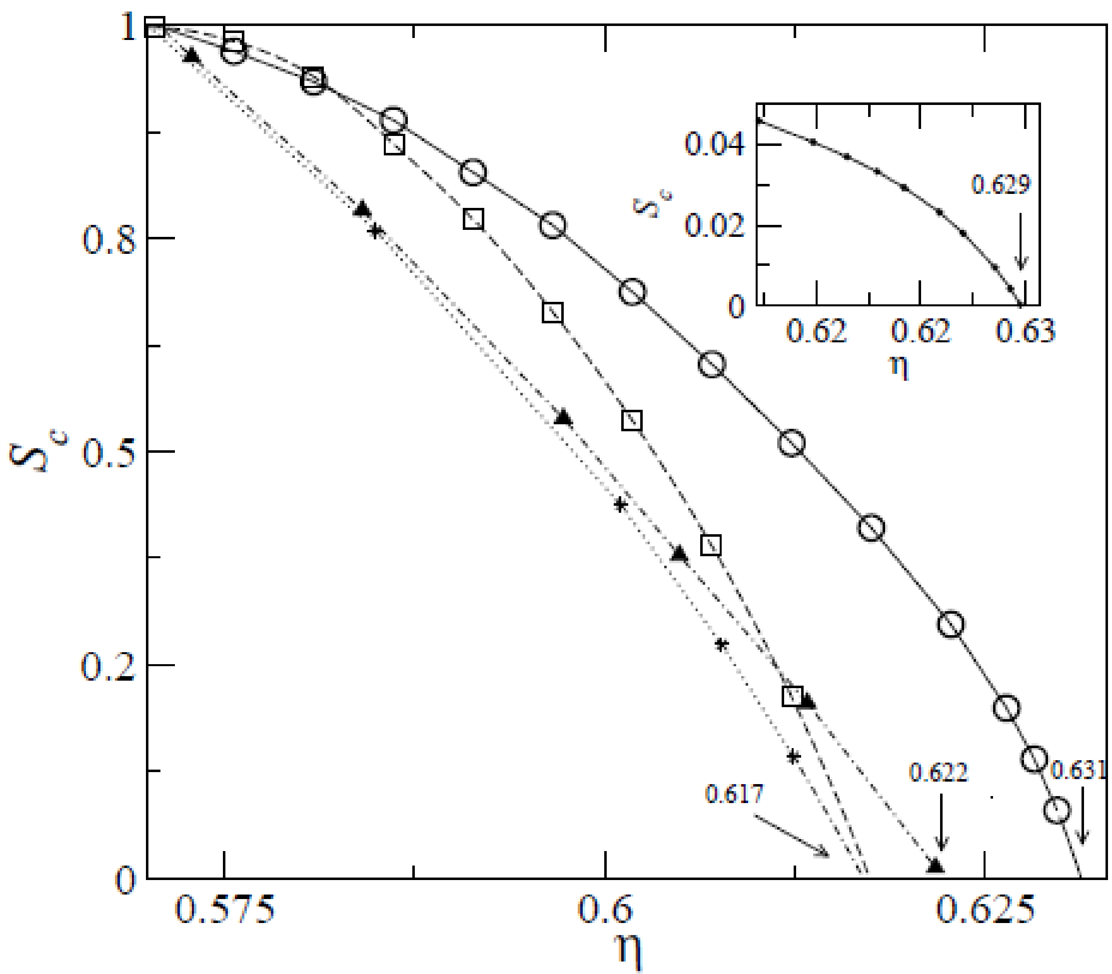
The hard sphere crystal mapped in to a low density fluid and free energy is calculated

The hard sphere system

$$\mathcal{S}_{\rm tot} = \frac{3}{2} - f_{\rm tot}$$

$$\mathcal{S}_c(\eta) = \mathcal{S}_{\rm tot}(\eta) - \mathcal{S}_{\rm vib}(\eta)$$

$$\mathcal{S}_{\rm vib}(\alpha) = s_{\rm id}(\alpha) - s_{\rm id}^0$$



Linking two Microscopic Models of a Supercooled Liquid based on its Structure and Dynamics

Premkumar, N. Bidhoodi and S.P. Das,
J. Chem. Phys. **144**, 124511 (2016)

$$\rho(\mathbf{r}) = \left(\frac{\alpha}{\pi}\right)^{3/2} \sum_{\{\mathbf{R}_i\}} e^{-\alpha(\mathbf{r}-\mathbf{R}_i)^2}$$

The density is parameterize in terms of the mass localization parameter α which is inversely proportional to square of the width of Gaussian profiles.

I. The average kinetic and potential energies of an oscillator with position x and momentum p are same and each equal to $K_B T/2$

$$\frac{\kappa_s < x^2 >}{2} = \frac{K_B T}{2} \quad \text{(I)}$$

$$< x^2 > = \frac{1}{2\,\alpha} \quad \text{(II)}$$

- The characteristics frequency of the oscillator is given by

$$\omega_0^2 = \frac{\kappa_s}{m} = 2 v_0^2 \alpha,$$

- v_0 - Thermal velocity
- κ_s - Spring constant

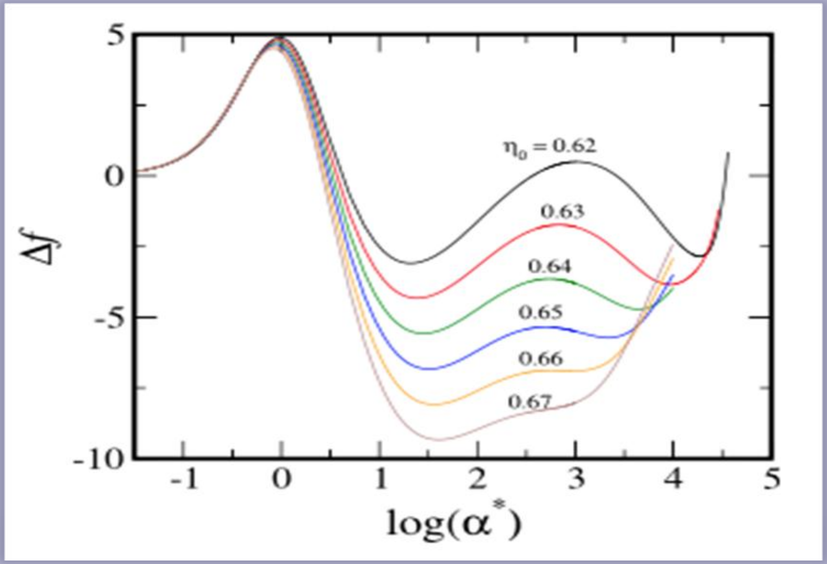
$$\phi(q,z) = \left[z - \frac{q^2 c_0^2}{z + i q^2 L(q,z)} \right]^{-1},$$

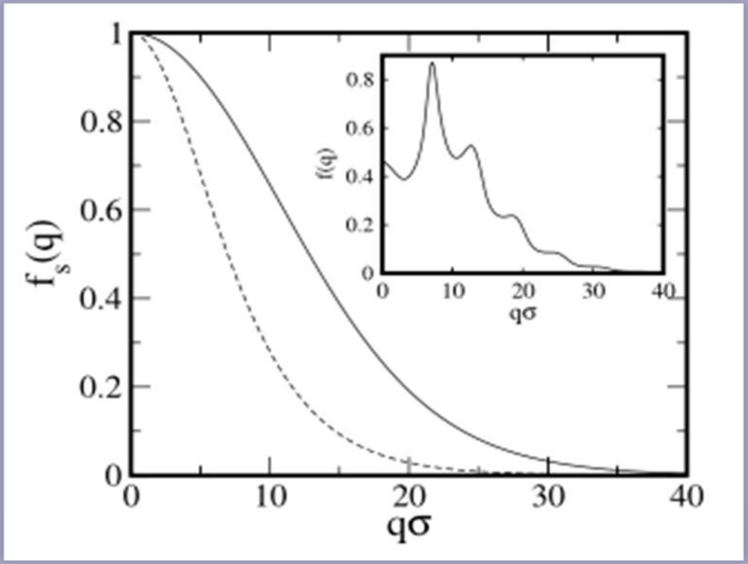
$$L(q,z) = L_0(q) + L^{mc}(q,z).$$

Numerical results:

DFT results: free energy surface and localization parameter

MCT results: long time dynamics of tagged particle at the transition point

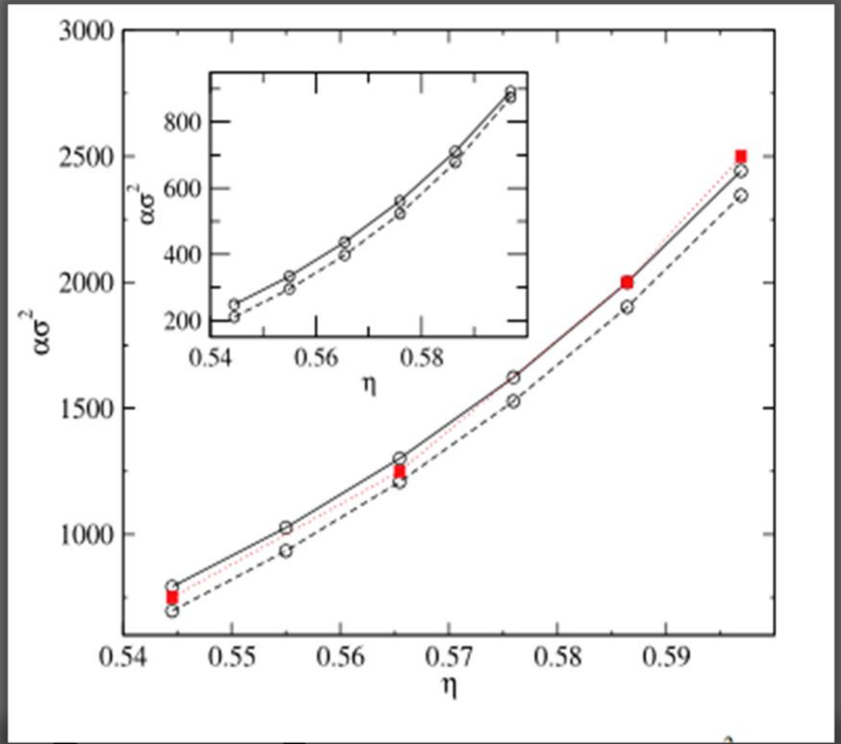




Free energy vs. α at fixed η=0.597 for different structures characterized in terms of the parameter η_0 as indicated with the corresponding curve.

Non-ergodicity parameters f_s for self and f for total correletion functions shown as the main and inset at η=0.525. In the main figure: solid line (present model) and dashed line [4]

➢ Mass localization parameters α_{DFT} and α_{MCT}



Higher order correlation functions and dynamic length scales

The four point correlation function

$$\lim_{t\to\infty} < \delta\rho(\mathbf{x},t)\delta\rho(\mathbf{x},0) >= \lim_{t\to\infty} < \psi(\mathbf{x},t) >= 0$$

Order parameter of the MCT.

$$\begin{aligned}\mathcal{G}_4(\mathbf{x},t) &= < \delta\rho(\mathbf{0},t)\delta\rho(\mathbf{0},0)\delta\rho(\mathbf{x},t)\delta\rho(\mathbf{x},0) > \\ &- < \delta\rho(\mathbf{0},t)\delta\rho(\mathbf{0},0) >< \delta\rho(\mathbf{x},t)\delta\rho(\mathbf{x},0) > \\ &= < \psi(\mathbf{0},t)\psi(\mathbf{r},t) > - < \psi(\mathbf{0},t) >< \psi(\mathbf{r},t) >\end{aligned}$$

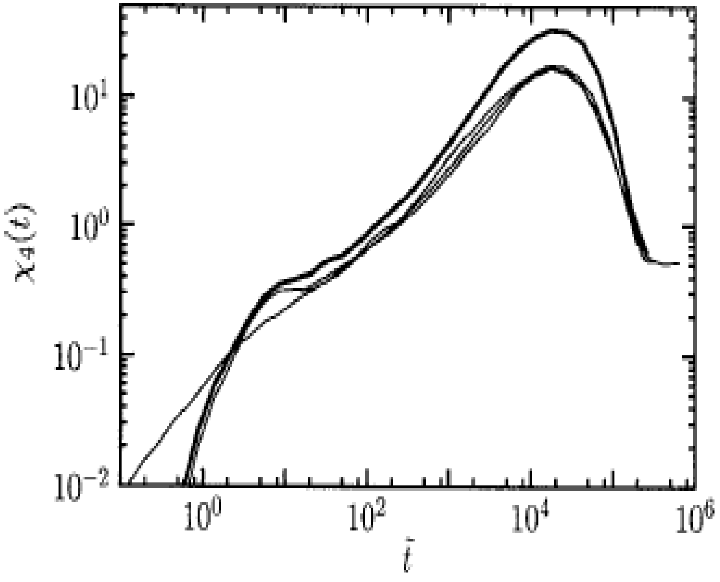
$$\phi(t) = \frac{1}{V}\int d\mathbf{x}\psi(\mathbf{x},t) \qquad V\left[< \phi^2(t) > - < \phi(t) >^2\right]$$

Four point correlation functions

(Berthier et. al., 2005, Dasgupta et. al. 2008)

$$F_s(\mathbf{k},t) = \left\langle \frac{1}{N_\alpha}\sum_{j=1}^{N_\alpha} e^{i\mathbf{k}\cdot[\mathbf{r}_j(t)-\mathbf{r}_j(0)]} \right\rangle, \quad = \quad \langle f_s(\mathbf{k},t)\rangle.$$

$$\chi_4(t) = N_\alpha[\langle f_s^2(\mathbf{k},t)\rangle - F_s^2(\mathbf{k},t)].$$



Dynamic correlation length identified

Numerical Solution of the Stochastic Equations (Sen Gupta, Das and Barrat, 2012)

- Simplest set of equations involving the density and the momentum $\rho(x,t)$ $g(x,t)$
- Discrete cubic lattice of small size 20^3
- Periodic boundary conditions
- Gaussian white noise

Noise correlation is described in terms of the dissipative tensor involving the shear and the longitudinal viscosity

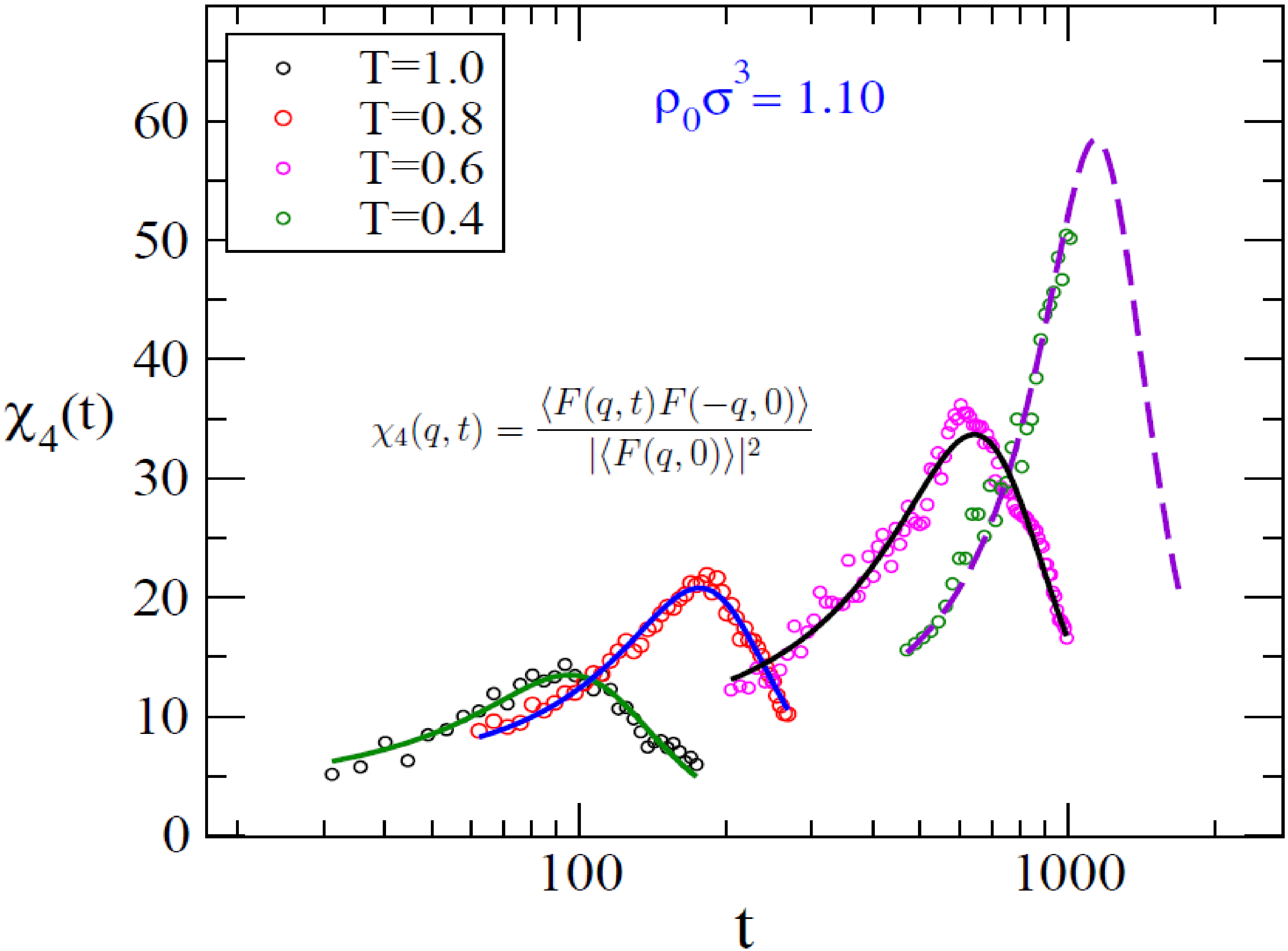
The Gaussian noise correlation is obtained in terms of bare transport coefficients for the system.

Bare transport matrix is adjusted so that the short time dynamics agrees with simulations.

The density and momentum fields are stored at the lattice points.

Results at suitably chosen time bins are saved to compute correlation functions.

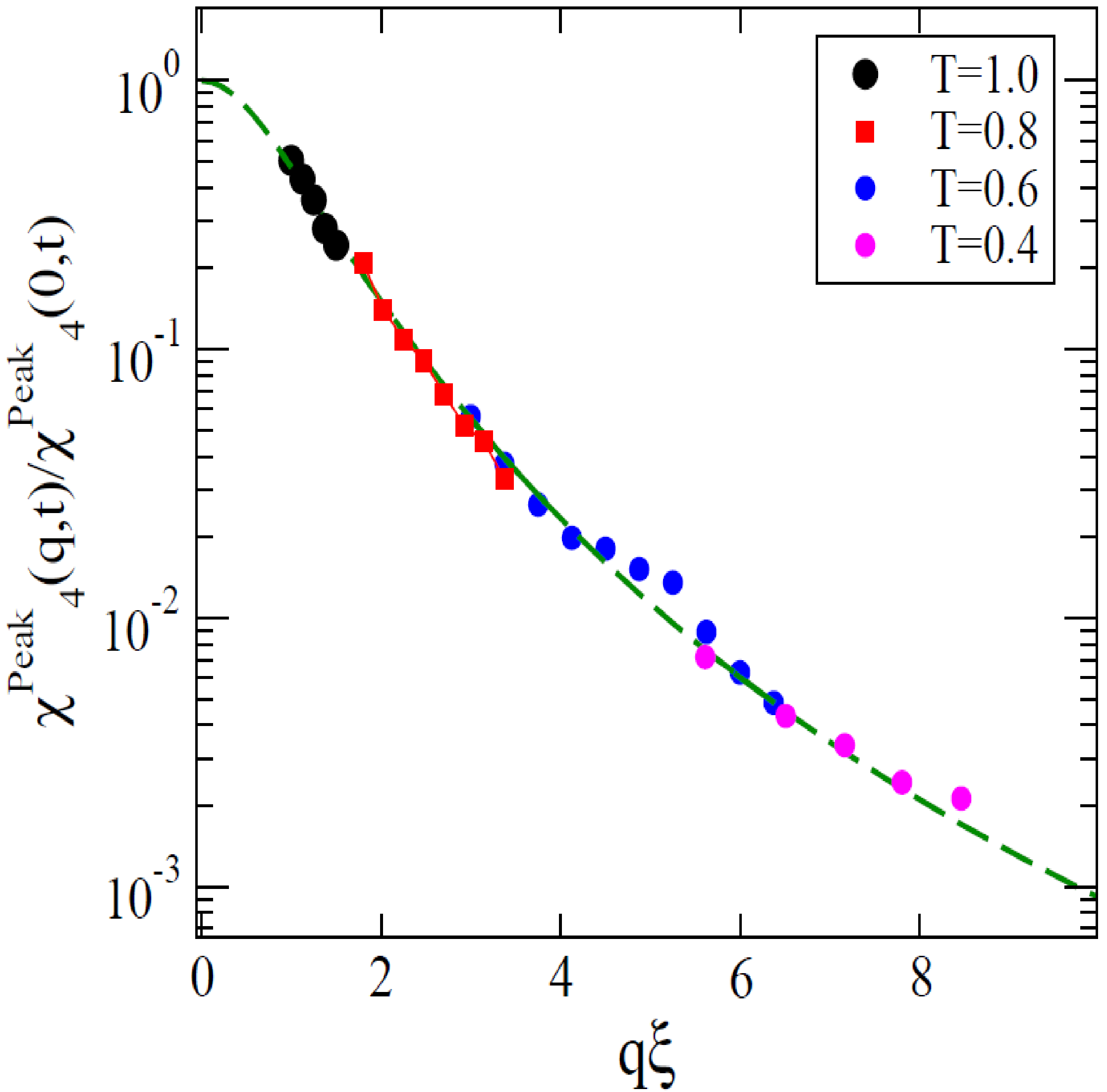
Both equilibrium and Non equilibrium correlations are studied



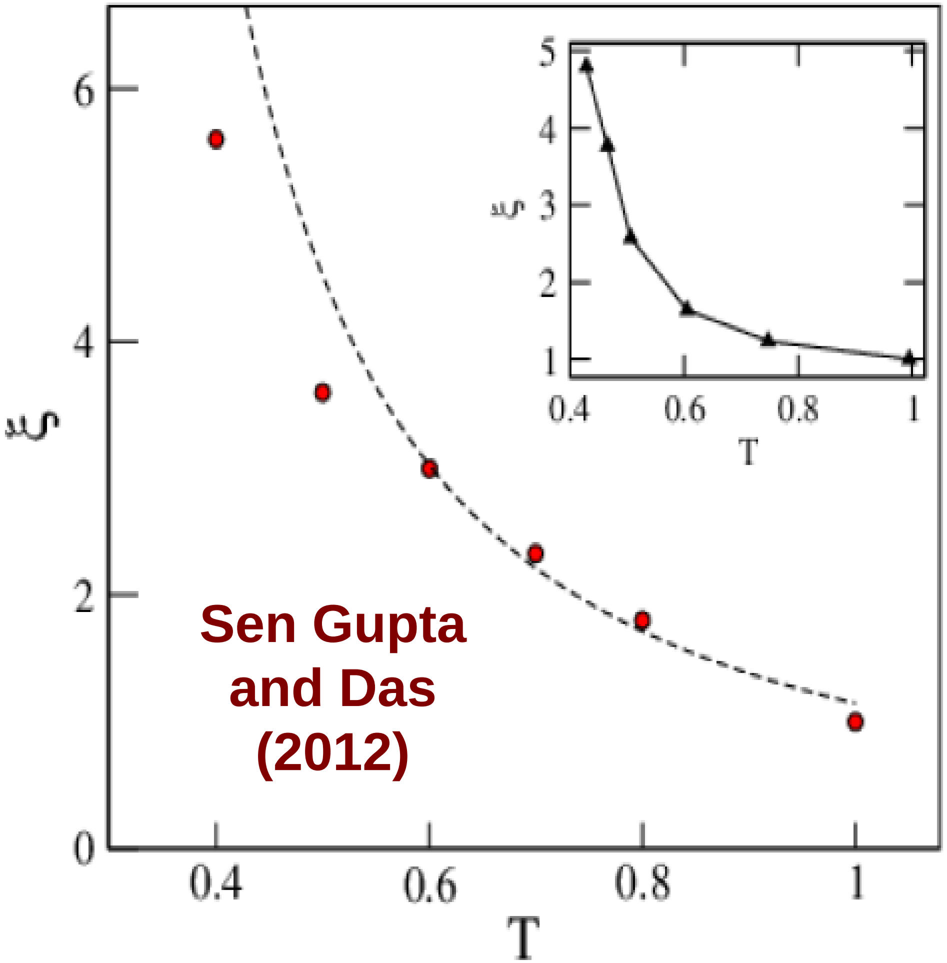
Sen Gupta and Das (2014))

The four point function

$$\chi_4(q,\tau_4,T) = \frac{\chi_4(0,\tau_4,T)}{1+(q\zeta(T))^2 + a_1(q\zeta)^4}$$



The dynamic length scale



Molecular dynamics simulations
Berthier et. al. 2007

No plateau in two point functions – but four point function displays the peak.
Dynamical Heterogeneities

Non Gaussian behavior

Four point function with collective density fluctuations : Measure of the departure from Gaussian approximation.

Four point correlation $\longrightarrow$

Product of two point correlation

(Beyond one loop approximation)

SUMMARY

ERGODIC-NONERGODIC TRANSITION BELOW FREEZING POINT.

EXTENSION OF LIQUID STATE DYNAMICS.

Role of fast decay of momentum fluctuations freezing of single particle dynamics – cage effect

Dynamic length scales from higher order correlations through

Direct solution of fluctuating hydrodynamic equations

Thank You !

New approach
(Field theory+ Kinetic theory)

Work with the equations of motion
Introduce the MSR fields at particle level

$$\dot{R}_i = \frac{P_i}{m}$$
$$\dot{P}_i = f_i$$

$$Z_N[H, h, \hat{h}] = \mathcal{N} \int \prod_{i=1}^{N} \mathcal{D}(\Psi_i) \mathcal{D}(\hat{\Psi}_i) d\Psi_i^{(0)}) P_0(\Psi_0) e^{-A_\Psi}$$
$$\times \exp(H \cdot \phi) \exp(h \cdot \Psi + i\hat{h} \cdot \hat{\Psi})$$

$$f_i = -\frac{\partial}{\partial R_i} U(R)$$

$$A = \int dt \sum_{i=1}^{N} \left[D\hat{R}_i^2(t) + i\hat{R}_i(t)[\dot{R}_i(t) - F_i(t) - R_0^i \delta(t - t_0)] \right]$$

Perturbation in terms of interaction potential. Noninteracting system at zeroth order

$$A = \sum_{i=1}^{N} A_i^0 + A_I$$

$$\bar{\rho}(x,t) = \sum_{i=1}^{N} \delta(x - R_i(t))$$

$$B(x,t) = -\sum_{i=1}^{N} \hat{\vec{P}}_i \cdot \frac{\partial}{\partial \vec{R}_i} \delta(x - R_i(t))$$

$$A_I = \int dt \int d^d x \int d^d y \; iB(x,t) \nabla_x V(x-y) \rho(y,t)$$

Linear Fluctuation-Dissipation Theorem (FDT)

for any function $f[\rho]$ the following FDT relation

$$G_{fB}(t-t') = \frac{i}{m} \theta(t-t') \beta \frac{\partial}{\partial t} G_{f\rho}(t-t')$$

Dyson Equation

$$G_{\rho\rho}(q,\omega) = -G_{\rho B}(q,\omega)\Gamma_{BB}(q,\omega)G_{B\rho}(q,\omega).$$

$$\Gamma_{BB}(q,\omega) = -2\pi\delta(\omega)\bar{\Gamma}(q) + \text{regular part.}$$

$$\frac{F(q)}{S(q)-F(q)} = S(q)\beta^2\bar{\Gamma}(q).$$

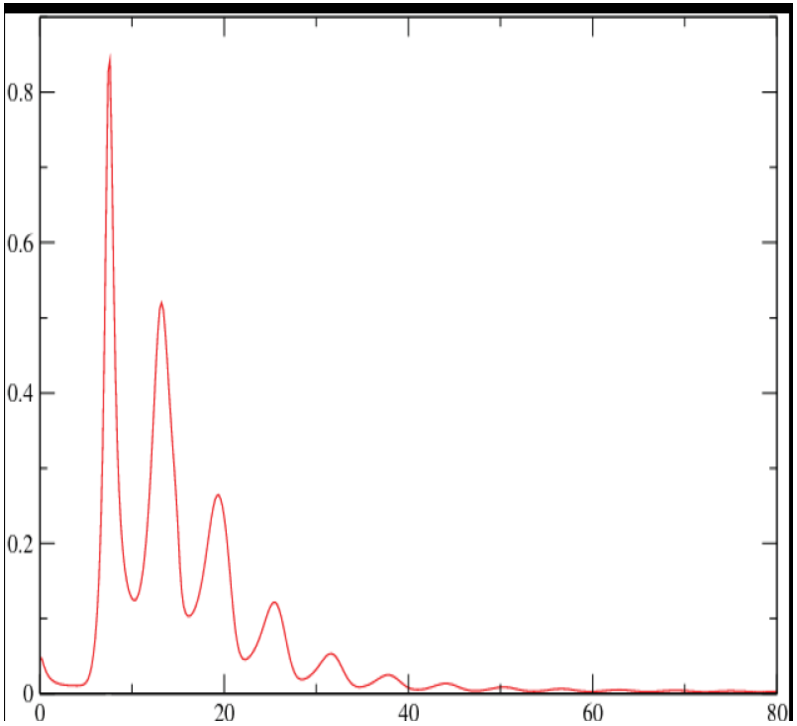
Similar equation as MCT without introducing the projection to slow modes : Perturbation theory in terms of the interaction potential.

The Ergodic-Nonergodic transition

$$\tilde{S}(q') = \frac{1}{1 + \tilde{V}(q') - M(q')},$$

where

$$M(q') = \rho_0 \beta \Gamma_{B\rho}(q,0)$$
$$= \frac{\pi}{12\eta} \int \frac{d^d k_3'}{(2\pi)^d} \frac{d^d k_4'}{(2\pi)^d} \delta(q_1' + k_3' + k_4')$$
$$\times \tilde{V}(k_3') \tilde{S}(k_3') \tilde{V}(k_4') \tilde{S}(k_4'),$$



ENE transtion at packing fraction .62

(Das and Mazenko, 2011)

Reorganizing the perturbation theory in terms of the effective potential

Brings the theory in better agreement with simulations